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EP 0 407 224 B1

Description

The present invention relates to novel polyphenylene ether polyamide blends having improved paint adhesion strength and excellent impact strength.

Specifically, polyphenylene ether polyamide blends containing at least one elastomeric material selected from ethylene- α -olefin-(diene) copolymers with a vinyl aromatic monomer and at least one unsaturated functional monomers selected from unsaturated nitrile monomers and alkyl(meth) acrylates grafted thereto as hereinafter defined, have improved impact strength and paint adhesion strength as compared to polyphenylene ether polyamide blends containing at least one ethylene- α -olefin-(diene) copolymer without such combination of unsaturated monomers grafted thereto, or containing at least one ethylene- α -olefin-(diene) copolymers with excessive quantity of such unsaturated functional monomers and vinyl aromatic monomers grafted thereto.

Blends of polyphenylene ether and polyamide have long been known. U.S.P. 3,379,792 taught improved processability of polyphenylene ethers by incorporating therein up to 25% by weight of polyamide.

Recently compatibility of such blends has been enhanced by incorporating therein a compatibilizing agent. U.S.P. 4,315,086 teaches the use of liquid diene polymers, epoxy compounds and compounds having in the molecule both (a) a carbon-carbon double bond or a carbon-carbon triple bond and (b) a carboxylic acid, acid anhydride, acid amide, imide, carboxylic acid ester, amino or hydroxyl group as compatibilizers. EP 46040 teaches copolymers of vinyl aromatic compounds and either an alpha, beta-unsaturated dicarboxylic acid anhydride or an imide compound thereof as a compatibilizer.

U.S.P. 4,659,763 teaches the use of quinone compounds, U.S.P. 4,600,741 teaches the use of trimellitic anhydride acid chloride and the like, U.S.P. 4,659,760 teaches the use of oxidized polyethylene wax, WO 85/05372 teaches the use of polycarboxylic acids such as citric acid, WO 87/07281 teaches the use of vinyl-trimethoxy silane as compatibilizers.

It has also been proposed to add various elastomeric materials to polyphenylene ether polyamide blends to enhance the impact strength.

Among many elastomeric materials, the use of ethylene- α -olefin copolymers and ethylene- α -olefinediene terpolymers are also proposed. U.S.P. 4,315,086 teaches the use of acrylic acid grafted ethylene-propylene copolymers. Japanese Kokai Patent TOKKAI SHO 63-33471 teaches the use of maleated ethylene-propylene-(diene) copolymers, TOKKAI SHO 63-205350 teaches the use of acrylonitrile/styrene grafted ethylene-propylene-(diene) copolymers, and TOKKAI SHO 63-312350 teaches the use of styrene grafted ethylene-propylene-(diene) copolymers.

While the use of ethylene- α -olefin-(diene) copolymers provides a certain advantage over other elastomeric materials to the polyphenylene ether polyamide blends as disclosed in those patents and patent applications, the polyphenylene ether polyamide blends with ethylene- α -olefin-(diene) copolymers incorporated shows minimal paint adhesion strength if no primer coating layer is applied to a substrate fabricated from those blends.

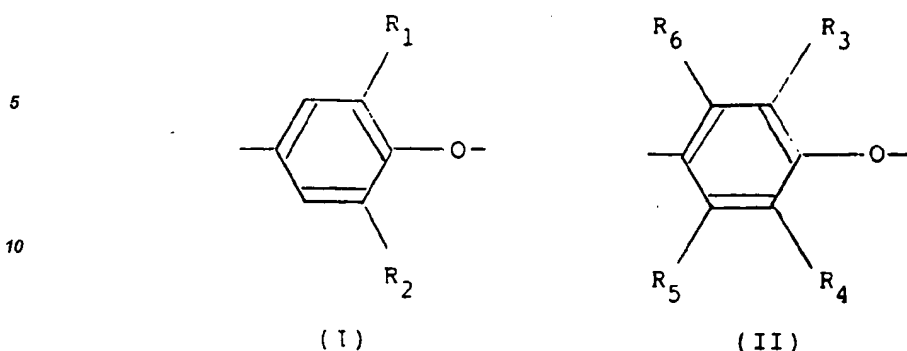
The use of styrene grafted ethylene- α -olefin-(diene) copolymers improves the paint adhesion strength over ungrafted ethylene- α -olefin-(diene) copolymers to some extent but not to a satisfactory level. The use of acrylonitrile/styrene grafted ethylene- α -olefin-(diene) copolymers were taught in TOKKAI SHO 63-205350. The impact strength of the blends, however, were poor due to the excessive content of styrene and acrylonitrile in the graftomers, although paint adhesion strength was excellent.

It is an objective of the present invention to provide a thermoplastic composition of enhanced paint adhesion and excellent impact strength, comprising polyphenylene ether, polyamide and ethylene- α -olefin-(diene) copolymer with a vinyl aromatic monomer and an unsaturated functional monomer grafted hereto, by optimizing the content of vinyl aromatic monomer and unsaturated monomer present in the graftomer as hereinafter disclosed.

According to the present invention, polyphenylene ether polyamide compositions having unexpectedly improved paint adhesion and high impact strength may be prepared by incorporating at least one elastomeric material selected from ethylene- α -olefin-(diene) copolymers with at least one vinyl aromatic monomer and at least one unsaturated functional monomer selected from unsaturated nitrile monomers and alkyl(meth)acrylates grafted thereto.

The compositions of the present invention are prepared from,

(A) from 5 to 95 parts by weight of at least one polyphenylene ether which is a homopolymer or copolymer comprising repeating unit I and optionally repeating unit II



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wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 are identical or different and each represents a monovalent residue with the proviso that R_3 and R_5 cannot be hydrogen simultaneously,

(B) from 95 to 5 parts by weight of at least one aliphatic polyamide and/or thermoplastic aromatic melt-polymerisable copolyamide comprising an aromatic amino acid and/or aromatic dicarboxylic acid,

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(C) from 5 to 50 parts by weight based on 100 parts by weight of the total of polyphenylene ether and polyamide, of at least one elastomeric material obtainable by graft copolymerisation of

(a) from 50 to 90% by weight of at least one ethylene- α -olefin-(diene) copolymer and

(b) from 50 to 10% by weight of a grafting monomer mixture comprising

(i) at least one vinyl aromatic monomer and

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(ii) at least one unsaturated functional monomer selected from unsaturated nitrile monomers and alkyl(meth)acrylates,

the total amount of unsaturated functional monomers being from 2 to 20% by weight of the total weight of the grafting monomer mixture, and

(D) from 0.01 to 30 parts by weight of at least one compatibilizing agent, based on 100 parts by weight of the total of the polyphenylene ether and polyamide.

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Especially preferred compatibilizing agents will be selected from the group consisting of

(a) liquid diene polymers,

(b) epoxy compounds,

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(c) unsaturated functional compounds having in the molecule both (a) at least one carbon-carbon double bond or carbon-carbon triple bond and (b) at least one carboxylic acid, acid halide, acid anhydride, acid amide, acid ester, imido, amino or hydroxyl group,

(d) aliphatic polycarboxylic acid compounds or the derivatives thereof having both (a) a group represented by the formula $-(OR)$ wherein R is hydrogen or an alkyl, aryl, acyl or carbonyl dioxy group and (b) at least two groups, each of which may be the same or different, selected from carboxylic acid, acid halide, acid anhydride, acid ester, acid amide, imide, amino and salts thereof, and

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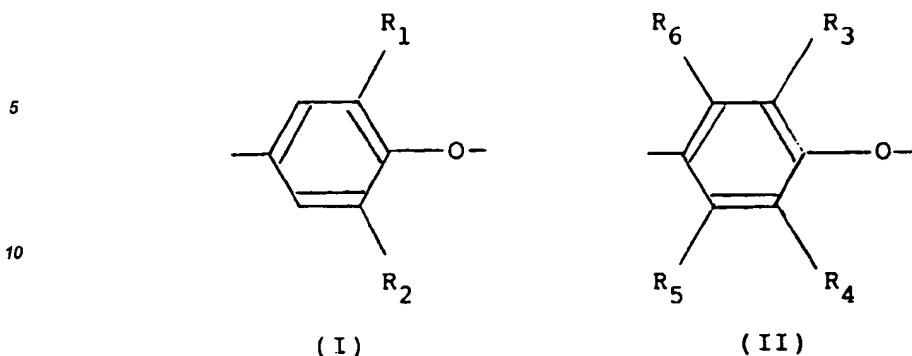
(e) polyfunctional acid halide compounds having both (a) an acid halide group and (b) a group selected from carboxylic acid, carboxylic acid anhydride, acid ester or acid amide.

The composition of the present invention will be prepared from 5 to 95, preferably 30 to 70% by weight polyphenylene ether (A), and from about 95 to 5, preferably 70 to 30% by weight polyamide (B), 5 to 50, preferably 5 to 30 parts by weight of at least one of the elastomeric materials as herein defined (C), based on 100 parts by weight of the total of the polyphenylene ether and polyamide, and from about 0.01 to 30, preferably from about 0.1 to about 5 parts by weight of at least one compatibilizer (D), based on 100 parts by weight of the total of the polyphenylene ether and polyamide. Preferably the polyamide (B) is present in an amount at least enough to form the continuous phase of the polyphenylene ether (A)/polyamide (B) blend.

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The polyphenylene ether component (A) used in the present invention is homopolymer or copolymer composed of the following repeating unit (I) or (I) and (II):

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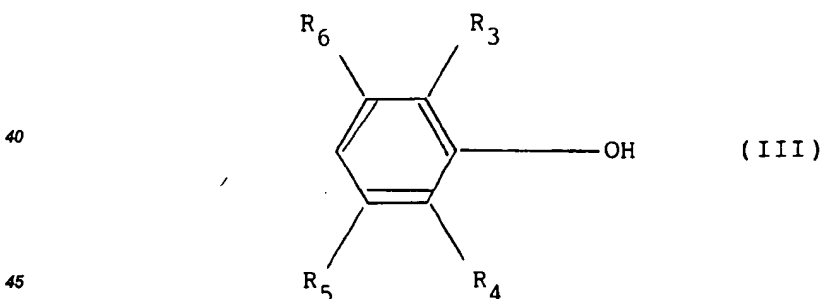
15 wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 which may be identical or different each represents a monovalent residue such as an alkyl group of 1 - 4 carbon atoms excluding tert-butyl group, an aryl group, a halogen atom or a hydrogen atom, and R_3 and R_5 cannot be simultaneously hydrogen atom.

20 The polyphenylene ether may be a mixture of said homopolymer and said copolymer, or a graft copolymer of said polymer with styrene.

The homopolymer of polyphenylene ether includes

poly(2,6-dimethyl-1,4-phenylene)ether,
 poly(2-methyl-6-ethyl-1,4-phenylene)ether,
 poly(2,6-diethyl-1,4-phenylene)ether,
 25 poly(2-ethyl-6-n-propyl-1,4-phenylene)ether,
 poly(2,6 di-n-propyl-1,4-phenylene)ether,
 poly(2-methyl-6-n-butyl-1,4-phenylene)ether,
 poly(2-ethyl-6-isopropyl-1,4-phenylene)ether,
 poly(2-methyl-6-chloro-1,4-phenylene)ether,
 30 poly(2-methyl-6-hydroxyethyl-1,4-phenylene)ether and
 poly(2-methyl-6-chloroethyl-1,4-phenylene)ether.

The copolymer of polyphenylene ether includes polyphenylene ether copolymers mainly composed of polyphenylene ether structure which is obtained by copolymerization with o-cresol or an alkyl-substituted phenol such as 2,3,6-trimethylphenol which is represented by the formula (III):



50 wherein R_3 , R_4 , R_5 and R_6 each represents a monovalent residue such as an alkyl group of 1 - 4 carbon atoms excluding tert-butyl group, an aryl group, a halogen atom or a hydrogen atom, and R_3 and R_5 cannot be simultaneously hydrogen atom.

Preferably the polyphenylene is poly (2,6-dimethyl-1,4-phenylene)ether, a copolymer of 2,6 dimethylphenol and 2,3,6-trimethylphenol, or a combination thereof.

55 The polyamide component (B) used in the present invention is well known in the art and may be selected from any of aliphatic polyamides or thermoplastic aromatic copolyamides or a combination thereof. The aliphatic polyamides have a molecular weight of 10,000 or more and can be produced by bonding of equimolar of a saturated aliphatic dicarboxylic acid of 4 - 12 carbon atoms and an aliphatic diamine of 2 - 12 carbon atoms. However, in the production, if necessary, the diamines may be excessively used so as to provide more amine terminal groups than carboxyl terminal groups in the polyamide, or alternatively, a dibasic acid may be exces-

sively used so as to provide more acid groups. Similarly, these polyamides can be conveniently produced from acid production derivatives and amine production derivatives such as esters, acid chlorides and amine salts, of the above mentioned acids and amines.

5 Typical examples of the aliphatic dicarboxylic acid used for the production of the polyamides include adipic acid, pimelic acid, azelaic acid, suberic acid, sebacic acid and dodecanedioic acid.

On the other hand, typical examples of the aliphatic diamines include hexamethylenediamine and octamethylenediamine.

In addition, the aliphatic polyamides may also be produced by self-condensation of lactam.

10 Examples of the aliphatic polyamides are polyhexamethylene adipamide (nylon 66), polyhexamethylene azelamide (nylon 69), polyhexamethylene sebacamide (nylon 610), polyhexamethylene dodecanamide (nylon 612), poly-bis-(p-aminocyclohexyl)methane dodecanamide, polytetramethylene adipamide (nylon 46) and polyamides produced by ring cleavage of lactam such as polycaprolactam (nylon 6) and polylauryl lactam. Furthermore, there may be used polyamides produced by polymerization of at least two amines or acids selected
15 from those used for the production of the above-mentioned polymers, for examples polymers produced from adipic acid, sebacic acid and hexamethylenediamine. The aliphatic polyamides further include blends of above-mentioned polyamides such as a blend of nylon 6 and nylon 66 including copolymers such as nylon 66/6.

Preferably, the aliphatic polyamides used in the present invention are polyhexamethylene adipamide (nylon 66), polycaprolactam (nylon 6) and a blend of polyhexamethylene adipamide (nylon 66) with polycaprolactam (nylon 6).

The thermoplastic aromatic copolyamide is a copolyamide containing an aromatic component therein, for example, polyhexamethylene isophthalamide (nylon 6I). The copolyamide containing an aromatic component therein means a melt-polymerizable polyamide containing as a main component an aromatic amino acid and/or
25 aromatic dicarboxylic acid such as para-aminomethylbenzoic acid, para-aminoethylbenzoic acid, terephthalic acid and isophthalic acid.

Diamines which may constitute another component of the polyamide include hexamethylenediamine, undecamethylenediamine, dodecamethylenediamine, 2,2,4-/2,4,4-trimethylhexamethylenediamine, m-xylylenediamine, p-xylylenediamine, bis(p-aminocyclohexyl)methane, bis(p-aminocyclohexyl)propane, bis(3-methyl-4-aminocyclohexyl) methane, 1,3-bis(aminomethyl)cyclohexane and 1,4-bis (aminomethyl)cyclohexane. An isocyanate may also be used in place of the diamine.

Any other comonomers may be used, if necessary. Examples of the comonomers are 4,4'-diphenylmethane diisocyanate and tolylene diisocyanate. Other examples thereof are a unit of lactam, a unit of ω -amino acid of 4 - 12 carbon atoms, a compound derived from an aliphatic dicarboxylic acid of 4 - 12 carbon atoms
35 and an aliphatic diamines of 2 - 12 carbon atoms, for example, lactams and amino acids such as ϵ -caprolactam, nonalolactam, 11-aminoundecanoic acid and 12-aminododecanoic acid, and equimolar salts of the above-mentioned various diamines and adipic acid, azelaic acid or sebacic acid.

Typical examples of the thermoplastic aromatic copolyamides comprising these components are copolymer polyamide of p-aminomethylbenzoic acid and ϵ -caprolactam (nylon AMBA/6), polyamides mainly composed of 2,2,4-/2,4,4-trimethylhexamethylenediamine-terephthalate (nylon TMDT and nylon TMDT/6I), polyamides mainly composed of hexamethylenediamine isophthalate and/or hexamethylenediamine-terephthalate and containing, as a comonomer, bis(p-aminocyclohexyl)methane-terephthalate, and/or bis(3-methyl-4-aminocyclohexyl)methane-isophthalate and/or bis(3-methyl-4-aminocyclohexyl)propane-isophthalate and/or
45 bis(p-aminocyclohexyl)propane-terephthalate (nylon 6I/PACM I, nylon 6I/DMPACM I, nylon 6I/PACP I, nylon 6I/6T/PACM I/PACM T, nylon 6I/6T/DMPACM I/DMPACM T, nylon 6I/6T/PACP I/PACP T), polyamides mainly composed of hexamethylenediamine-isophthalate or hexamethylenediamine-terephthalate and containing, as a comonomer, ϵ -caprolactam, 12-aminododecanoic acid, hexamethylenediamine-adipate, bis(p-aminocyclohexyl) methane-adipate or bis(3-methyl-4-aminocyclohexyl) methane-adipate (nylon 6I, 6I/6T, 6I/12, 6T/6, 6T/66, 6I/PACM 6, 6I/DMPACM 6), and polyamides mainly composed of bis(p-aminocyclohexyl)methane-isophthalate or bis(3-methyl-4-aminocyclohexyl)methane-isophthalate and containing, as a comonomer, hexamethylenediamine-dodecanedioate or 12-aminododecanoic acid (nylon PACM I/612 and nylon DMPACM I/12).

The aromatic nuclear-hydrogenated copolyamide of component (B) is an alicyclic copolyamide obtained by using cyclohexane-1,4-dicarboxylic acid or cyclohexane-1,3-dicarboxylic acid obtained by nuclear-hydrogenation of terephthalic acid or isophthalic acid in place of terephthalic acid or isophthalic acid which is an acid
55 component of the above-mentioned aromatic copolyamides. Furthermore, nuclear-hydrogenation product of diamines or diisocyanates such as 4,4'-diphenylmethane diisocyanate or tolylene diisocyanate, may also be used as a monomer.

The ethylene α -olefin (diene) copolymers useful for the practice of the present invention are well known

in the art. The illustrative examples of the ethylene α -olefin (diene) copolymers include ethylene propylene copolymer often called EPR, ethylene propylene 1,4-hexadiene copolymer, ethylene propylene dicyclopentadiene copolymer, ethylene propylene ethylidene norbornene copolymer collectively often called EPDM, ethylene butene-1 copolymer, and ethylene butene-1 ethylidene norbornene copolymer.

The term "unsaturated nitrile monomers" used herein means a compound having in its molecular structure at least one ethylenic carbon-carbon double bond or carbon-carbon triple bond and -CN radical. The preferred unsaturated nitrile monomers are acrylonitrile and methacrylonitrile. The most preferred unsaturated nitrile monomer is acrylonitrile.

Alkyl(meth)acrylates useful for the practice of the present invention are well known in the art. The illustrative example of alkyl(meth)acrylates include methylmethacrylate, ethylmethacrylate, butylmethacrylate, glycidylmethacrylate, 2-ethylhexylmethacrylate, methylacrylate, ethylacrylate, and butylacrylate.

The elastomeric material components (C) used for the practice of the present invention may be prepared by grafting at least one vinyl aromatic monomer and at least one of unsaturated nitrile monomers and/or alkylmethacrylates to at least one of ethylene- α -olefin (diene)-copolymers.

Method for grafting of such monomers to the ethylene- α -olefin-(diene) copolymers is not critical in the practice of the present invention and any known method in the art may be employed. Melt mixing of the ethylene- α -olefin-(diene) copolymers and the grafting monomers with a suitable amount of a free radical initiator may be employed. Grafting of the said monomers under an aqueous suspension of ethylene α -olefin (diene) copolymers with a suitable amount of a free radical initiator and a dispersing agent may also be employed.

In case the content of the unsaturated nitrile monomers and/or alkyl(meth)acrylate(s) in the total of the vinyl aromatic monomer and the unsaturated functional monomer(s) grafted to the ethylene α -olefin (diene) copolymer exceeds about 20% by weight, the impact strength of the polyphenylene ether polyamide blends decreases.

In case the content of the unsaturated nitrile monomer(s) and/or alkyl(meth)acrylate(s) by the same measure is lower than about 2% by weight, the paint adhesion strength is improved only marginally.

In case the content of the total of the unsaturated monomers grafted to the ethylene- α -olefin-(diene) copolymer in the said unsaturated monomer co-grafted ethylene- α -olefin-(diene) copolymer (hereinafter referred to as Graft Rubber) exceeds about 50% by weight, the impact strength of the polyphenylene ether polyamide composition goes down remarkably.

In case the content of the total of the unsaturated monomers grafted in Graft Rubber is lower than about 10% by weight, the paint adhesion strength is improved only marginally.

The amount of Graft Rubber will be from about 5 to 50, preferably 5 to 30 parts by weight per 100 parts by weight of the polyphenylene ether polyamide blends.

Graft rubbers may further be functionalized with an unsaturated functional monomer including, but not limited to, maleic anhydride, fumaric acid, glycidylmethacrylate, acrylamide and the like.

It is within the scope of the present invention to add copolymers of unsaturated nitrile monomers such as acrylonitrile styrene copolymer often called SAN and/or alkyl(meth)acrylate polymers such as polymethylmethacrylate and methylmethacrylate butylacrylate copolymer to further enhance the paint adhesion strength if the need may be.

Examples of preferred compatibilizing agents (D), that may be employed in the practice of the present invention are

- (a) liquid diene polymers,
- (b) epoxy compounds,
- (c) unsaturated functional compounds,
- (d) aliphatic polycarboxylic acid compounds or the derivatives thereof as described hereunder, and
- (e) polyfunctional acid halide compounds as described hereunder.

Liquid diene polymers suitable for use herein include homopolymers of a conjugated diene and copolymers of a conjugated diene with at least one monomer selected from the group consisting of other conjugated dienes, vinyl monomer, e.g., ethylene, propylene, butene-1, isobutylene, hexene-1, octene-1 and dodecene-1, and mixtures thereof, having a number average molecular weight of from 150 to 10,000, preferably 150 to 5,000. These homopolymers and copolymers include, among others, polybutadiene, polyisoprene, poly(1,3-pentadiene), poly(butadiene-isoprene), poly(styrene-butadiene), polychloroprene, poly(butadiene- α methyl styrene), poly(butadiene-styrene-isoprene), and poly(butylene-butadiene).

Epoxy compounds suitable for use in the practice of the present invention there are given (1) epoxy resins produced by condensing polyhydric phenols (e.g. bisphenol-A, tetrabromobisphenol-A, resorcinol and hydroquinone) and epichlorohydrin; (2) epoxy resins produced by condensing polyhydric alcohols (e.g. ethylene glycol, propylene glycol, butylene glycol, polyethylene glycol, polypropylene glycol, pentaerythritol and trimethylolthane) and epichlorohydrin; (3) glycidyletherified products of monohydric compounds including phenyl gly-

cidylether, allyl glycidylether, butyl glycidylether and cresyl glycidylether; (4) glycidyl derivatives of amino compounds for example, the diglycidyl derivative of aniline, and (5) epoxidized products of higher olefinic or cycloalkene, or natural unsaturated oils (e.e. soybean oil) as well as of the foregoing liquid diene polymers.

- 5 The unsaturated functional compounds are those having in the molecule both (a) an ethylenic carbon-carbon double bond or a carbon-carbon triple bond and (b) at least one carboxylic acid, acid anhydride, acid halide, anhydride, acid halide anhydride, acid amide, acid ester, imide, amino, or hydroxy group. Examples of such unsaturated polyfunctional compounds are maleic acid; maleic anhydride; fumaric acid; citraconic acid; itaconic acid; maleimide; maleic hydrazide; reaction products resulting from a diamine and maleic anhydride, 10 maleic acid, fumaric acid, etc.; dichloromaleic anhydride; maleic acidamide; unsaturated monocarboxylic acid (such as acrylic acid, butenoic acid, methacrylic acid, α -ethylacrylic acid, pentenoic acid, decenoic acids, undecenoic acids, dodecenoic acids, linoleic acids); esters, acid amides or anhydrides of the foregoing unsaturated carboxylic acids including glycidyl(meth) acrylate; unsaturated alcohols (such as allyl alcohol, crotyl alcohol, methyl vinyl carbinol, 4-pentene-1-ol, 1,4-hexadiene-3-ol, 3-butene-1,4-diol, 2,5-dimethyl-3-hexene- 15 2,5-diol and alcohols of the formulas $C_nH_{2n-6}OH$, $C_nH_{2n-7}OH$ and $C_nH_{2n-9}OH$, wherein n is a positive integer up to 30), unsaturated amines resulting from replacing the -OH group(s) of the above unsaturated alcohols with NH_2 groups; and functionalized diene polymers and copolymers.

The aliphatic polycarboxylic acid compounds or the derivatives thereof suitable are represented by the formula:



- 20 wherein R is a linear or branched chain, saturated aliphatic hydrocarbon of from 2 to 20, preferably 2 to 10 carbon atoms; R^I is selected from the group consisting of hydrogen or an alkyl, aryl, acyl or carbonyl dioxo group of 1 to 10, preferably 1 to 6, most preferably 1 to 4 carbon atoms, especially preferred is hydrogen; each R^{II} is independently selected from the group consisting of hydrogen or an alkyl or aryl group of from 1 to 20 25 carbon atoms, preferably from 1 to 10 carbon atoms; each R^{III} and R^{IV} is independently selected from the group consisting essentially of hydrogen or an alkyl or aryl group of from 1 to 10, preferably from 1 to 6, most preferably 1 to 4 carbon atoms; m is equal to 1 and (n + s) is greater than or equal to 2, preferably equal to 2 or 3, and n and s are each greater than or equal to zero and wherein (OR^I) is alpha or beta to a carbonyl group and at least two carbonyl groups are separated by 2 to 6 carbon atoms. Obviously, R^I , R^{II} , R^{III} and R^{IV} cannot 30 be aryl when the respective substituent has less than 6 carbon atoms.

Illustrative examples of suitable polycarboxylic acids are citric acid, malic acid, and agaricic acid.

- The polyfunctional acid halide compounds suitable for use herein are characterized as having both (a) at least one acid halide group, preferably acid chloride group and (b) at least one carboxylic acid, carboxylic acid anhydride, acid ester or acid amide group, preferably a carboxylic acid or carboxylic acid anhydride group. Ex- 35 amples of compatibilizers within this group are trimellitic anhydride acid chloride, and chloroformyl succinic anhydride.

- The total amount of one or more of the compatibilizing agent used herein will be dependent on the specific compatibilizing agent selected. It is desirable to use at least necessary enough amount in enhancing the compatibility of the polyphenylene ether polyamide blend. Generally the amount of compatibilizing agent will be 40 from about 0.01 to 30, preferably from about 0.1 to about 5 parts by weight per 100 parts by weight of the polyphenylene ether polyamide blend.

- Blending method of the components (A), (B), (C) and (D) is not critical. Known melt kneading methods can be employed as the blending method. Extruders, kneaders, rolls and the like may be used. Preferably extruders can be used as melt kneading apparatuses. There is no special limitation in sequence of addition 45 of the components upon melt kneading. That is, there are a method which comprises adding all of the components (A), (B), (C) and (D), at the same time and simultaneously melt-kneading them and a method which comprises pre-melt-kneading components (A), (C) and (D) in the presence or absence of a free-radical initiator and then adding component (B) and melt-kneading them. It should be noted, however, that compatibilizer and if employed, a free radical initiator must always be melt kneaded with all or a part of polyphenylene ether.

- 50 The foregoing polyphenylene ether polyamide blends may further comprise inorganic fillers such as talc, aluminosilicate, mica, carbon black, and glass fiber, pigments, heat stabilizers, ultraviolet degradation inhibitors, antioxidants, flame retardants, and plasticizers.

The molded products obtained from the thermoplastic resin composition of the present invention can be used suitably for automobile parts and electrical and electronic parts.

- 55 As examples of automobile parts to which the composition of the present invention can be applied, mention may be made of exterior trim parts such as bumper, fender, apron, hood panel, fascia, rocker panel, rocker panel reinforce, floor panel, rear quarter panel, door panel, door support, roof top, and trunk lid, interior trim parts such as instrument panel, console box, glove box, shift knob, pillar garnish, door trim, handle, arm rest, wind louver, carpet, seat belt, and seat, interior parts of engine room such as distributor cap, air cleaner, radiator

tank, battery case, radiator shroud, washer tank, cooling fan, and heater case, mirror body, wheel cover, trunk trim, and trunk mat.

The following examples further illustrate the present invention, but the present invention is not limited to them.

(Preparation of Graft Rubber)

Graft Rubbers used in the examples or comparative examples herein were prepared in the following manner;

1) Graft Rubber A (a styrene/acrylonitrile grafted EPDM)

A styrene/acrylonitrile grafted EPDM was prepared by suspension graft copolymerization.

A styrene/acrylonitrile grafted EPDM obtained contained 24.7 wt% of styrene component, 1.5 wt% of acrylonitrile component.

The content of acrylonitrile monomer in the total of polymerized styrene and acrylonitrile was 5.7 wt%.

2) Graft Rubber B

Graft Rubber B was prepared in the same manner as in the preparation of Graft Rubber A except that EPDM was substituted with EPR (Sumitomo Chemical Co., Ltd.'s Esprene E-100).

3) Graft Rubber C

Graft Rubber C was prepared in the same manner as in the preparation of Graft Rubber A except that acrylonitrile was substituted with methylmethacrylate.

4) Graft Rubbers D through J

Graft Rubbers D through J were prepared in the same manner as in the preparation of Graft Rubber A except that the quantity of styrene and acrylonitrile charged were changed as shown in each column of Table-I, and that the quantity of benzoyl peroxide was adjusted in proportion to the total quantity of styrene and the functional monomer.

The content of ethylene α -olefin (diene) copolymer in Graft Rubbers and the content of the functional monomer in the total of polymerized styrene and the polymerized functional monomer present in Graft Rubbers were shown in Table-I.

(Preparation of polyphenylene ether polyamide blends)

In the preparation of the polyphenylene ether polyamide blends disclosed in the example herein, a twin screw extruder TEX44 made by Nippon Seikoshō Kabushiki Kaisha was used.

The extruder had L/D ratio of 32 and was equipped with a first feed opening at the position of L/D ratio of 1 and with a second feed opening at the position of L/D ratio of 16. (L: the length of the screw, D: the diameter of the screw).

The cylinder temperature was set at about 260°C and screw speed was set at 360 rpm. The formulation of the individual blend was shown in Table-II. The paint adhesion strength and Izod Impact Strength measured of each blend were also shown in Table-II.

In Table-II, compatibilizer and free radical initiator were shown in parts by weight per 100 parts of the total of the polymeric materials and each of the polymeric materials was shown in weight % of the total of the polymeric materials.

The ingredients listed in the column "Feed-1" of Table-II were fed from the first feed opening. The ingredients listed in the column "Feed-2" of Table-II were fed from the second feed opening. All ingredients fed together either from the first feed opening or the second feed opening were mixed well by a tumbler mixer prior to the feeding.

The feed rate of the first feed and the second feed were controlled by the automatic weight feed control system so as to maintain the formulation of the individual blend as specified in Table-II.

The polyphenylene ether employed in the examples was either polyphenylene ether having a reduced viscosity of 0.52 dl/g (hereinafter denoted as PPE-A) or polyphenylene ether having a reduced viscosity of 0.42 dl/g (hereinafter denoted as PPE-B) measured at 25 °C in a chloroform solution of 0.5 g/dl concentration manufactured by Nippon Polyether Kabushiki Kaisha.

The polyamide 6, if employed, was Unitika Kabushiki Kaisha's Nylon 6 A1030 BRL throughout the examples. The polyamide 66, if employed, was UBE Kosan Kabushiki Kaisha's UBE nylon 66 2015B.

The aromatic polyamides in the examples, if employed, was Huels AG's Trogamid® T 2010.

Polymethylmethacrylate, if employed in any of the examples was Sumitomo Chemical Co., Ltd.'s Sumipex® LG. Acrylonitrile styrene copolymer, if employed in any of the examples was Sumitomo Naugatuck Co., Ltd.'s

Clearpet ® 1,000.

The free radical initiator, if employed, was dicumyl peroxide, Sanperox® DCP made by Sanken Kako Kaishiki Kaisha. The free radical initiator, if employed, was always preblended with polyphenylene ether and fed from the first feed opening. Polyphenylene ether was always fed from the first feed opening and polyamides were always fed from the second opening.

The paint adhesion test was performed in the following manner;

- 1) The granules of each of the blends prepared according to the formulation listed in Table-II to be tested were always dried at 100 °C for 6 hours with preheated dry air stream, the dew point of which was about -40 °C, and cooled thereafter by room temperature dry air stream.
- 2) The blend granules were injection molded to form a test plates of 150 mm x 150 mm x 3 mm size at a temperature range of about 290 °C.
- 3) The resulting plates were subjected to a paint spray utilizing a paint spray gun to form a paint layer of about 25 micron.
- 4) The paint coated plates were then cured for 30 minutes at 70 °C in a infrared paint cure oven.
- 5) The paint layer peeling test was performed, 2 hr, 5 hr, 12 hr and 24 hr after the paint curing.

The cured paint layer was cross cut by a sharp edged knife so as to make one hundred of 2 mm by 2 mm square pieces of the layer. Then a sheet of adhesive tape was applied on to the cross cut surface and the tape was peeled off.

The paint adhesion strength was measured by counting the number of about 2 mm by 2 mm square pieces remained unpeeled off, out of the 100 cross cut pieces.

6) The paint used in the examples was "Origiplat Z-NY metallic silver" manufactured by Origin Denki Kaishiki Kaisha.

The impact strength of the blends were measured in terms of Izod Impact Strength according to the method specified in ASTM D-256.

Example-1

20 Kg of polyphenylene ether (PPE-A), 0.25 kg of maleic anhydride (MAH), 5 g of dicumylperoxide (DCP), and 5 kg of Graft Rubber A were premixed as prescribed in the Feed-1 column of Example-1 of Table-II, using a 100 liter tumbler mixer blending the ingredients for 30 minutes prior to the feeding to the first feed opening of the TEX-44 twin screw extruder.

The premix prepared for the first feed opening will be referred to as the first feed premix hereinafter. 20 Kg of the nylon 6 and 5 kg of the nylon 66 were premixed as prescribed in the Feed-2 column of Example-1 of Table-II using the same tumbler mixer for 30 minutes prior to the feeding to the second feed opening of the TEX-44 twin screw extruder.

The premix prepared for the second feed opening will be referred to as the second feed premix hereinafter. The cylinder temperature of the extruder was set at about 260 °C and the screw speed, at about 360 rpm. The first feed premix was fed to the first feed opening at a rate of 20.2 kg/hr and the second feed premix was fed to the second feed opening at a rate of 20 kg/hr so as to maintain the formulation of the ingredients shown in Example-1.

The resulting blend was cooled in a water bath by chilled water about 10 °C and pelletized and dried. Thus prepared blend granules were injection molded to make 5 plates of 150 mm x 150 mm x 30 mm test specimen.

The abarage of the paint adhesion strength measured of the five plates was shown in the Table-II. Izod Impact Strength measured was also shown in Table-II.

Example-2

The experiment was conducted in the same manner as in Example-1 except that Graft Rubber A was substituted with Graft Rubber B.

Example-3

The experiment was conducted in the same manner as in Example-1 except that Graft Rubber A was substituted with Graft Rubber C and the blend of polyamide 6 and polyamide 66 was substituted with polyamide 6, as shown in Example-3 of Table-II.

Example-4

5 The experiment was conducted in the same manner as in Example-2 except that 1 kg out of 20 kg of poly-phenylene ether was substituted with PMMA, as shown in Example-4 of Table-II.

Example-5

10 The experiment was conducted in the same manner as in Example-4 except that PMMA was substituted with the same amount of acrylonitrile styrene copolymer (SAN) as shown in Example-5 of Table-II.

Comparative Example-1

15 The experiment was conducted in the same manner as in Example-1 except that Graft Rubber A was substituted with Graft Rubber F.

Comparative Example-2

20 The experiment was conducted in the same manner as in Example-1 except that Graft Rubber A was substituted with Graft Rubber G.

Examples-6 through 7 and Comparative Examples-3 through 7

25 The experiments were conducted in the same manner as in Example-1 except that;
(1) about 20.2 kg each of the first feed premix was prepared according to the formulation shown in Feed-1 column of each of the examples, and evenly charged to the first feed opening of the extruder at a rate of 20.2 kg/hr.
(2) 20 kg each of the second feed premix was prepared according to the formulation shown in Feed-2 column of each of the examples, and evenly charged to the second feed opening of the extruder at a rate of
30 20 kg/hr.

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Table-I

Graft rubber	Analytical Result of Graft Rubbers		
	Ethylene α -olefin copolymer wt%	AN ⁽¹⁾ wt% ⁽³⁾	MMA ⁽²⁾ wt% ⁽³⁾
A	75.3	5.7	-
B	76.0	4.8	-
C	74.9	-	5.6
D	89.6	4.9	-
E	61.2	12.5	-
F	71.0	-	-
G	75.2	27.7	-
H	60.5	22.4	-
I	35.2	8.1	-
J	96.0	7.5	-

(1) Acrylonitrile (2) methylmethacrylate

(3) calculated by the formula:

$$100 \times \text{AN(MMA)} / [\text{AN(MMA)} + \text{styrene}]$$

Table-II-(1)

		Example (EX) 1	EX 2	EX 3	EX 4	EX 5	Compar- ative EX 1
Feed-1	PPE-A	40	40	40	38	38	40
	PPE-B	-					
	Compatibilizer	MAH* 0.5	MAH* 0.5	MAH* 0.5	MAH* 0.5	MAH* 0.5	MAH* 0.5
	Free radical initiator	0.01	0.01	-	-	-	-
	Graft rubber	A 10	B 10	C 10	B 10	B 10	F 10
	PMMA	-	-	-	2	-	-
	SAN	-	-	-	-	2	-
Feed-2	Nylon 6	40	40	50	50	50	50
	Nylon 66	10	10	-	-	-	-
	Aromatic polyamide (Trogamid)	-	-	-	-	-	-
	Izod Impact Strength (ASTM D-256)						
	23°C (kg·cm/cm)	22	23	46	41	39	48
	-30°C (") (3.2 t)	10	10	12	11	10	12
	Paint						
	adhesion 2 hr	52	46	15	82	95	0
	strength 5 hr	80	73	49	94	99	23
	12 hr	96	94	89	99.4	100	41
	24 hr	100	99.9	99.2	100	100	59

* Maleic anhydride

5

Table-II-(2)

		Compar- ative EX 2	EX 6	Compar- ative EX 3	EX 7	Compar- ative EX 4	
10							
15	Feed-1	PPE-A	40	-	-	40	40
		PPE-B		35	35	-	-
20		Compatibilizer	MAH*	Citric acid 0.5	Citric acid 0.5	Fumaric acid 0.5	Fumaric acid 0.5
		Free radical initiator	-	-	-	0.01	0.01
25		Graft Rubber	G 10	D 15	J 15	E 10	H 10
		PMMA	-	-	-	-	-
		SAN	-	-	-	-	-
30	Feed-2	Nylon 6	50	50	50	50	50
		Nylon 66	-	-	-	-	-
35		Aromatic polyamide (Trogamid)	-	-	-	-	-
40		Izod Impact strength (ASTM D-256)					
		23°C (kg·cm/cm)	13	27	29	38	10
45		-30°C (") (3.2 t)	8.3	12	13	7.5	7
		Paint					
		adhesion 2 hr	75	12	0	63	72
		strength 5 hr	91	40	22	85	90
50		12 hr	99.9	85	51	98	99.7
		24 hr	100	99.0	74	100	100

* Maleic anhydride

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Table-II-(3)

5			Compar- ative EX 5	Compar- ative EX 6	EX 8	Compar- ative EX 7
10		PPE-A	40	40	40	40
		PPE-B	-	-	-	-
15		Compatibilizer	MAH* 0.5	MAH* 0.5	MAH* 0.5	MAH* 0.5
	Feed-1	Free radical initiator	0.01	0.01	-	-
20		Graft Rubber	I 10	mEPR** 10	C 10	F 10
25		PMMA	-	-	-	-
		SNA	-	-	-	-
30		Nylon 6	50	50	45	45
	Feed-2	Nylon 66	-	-	-	-
35		Aromatic polyamide (Trogamid)	-	-	5	5
40		Izod Impact strength (ASTM D-265)				
		23°C (kg·cm/cm)	10	57	45	46
45		-30°C (") (3.2 t)	4.5	13	11	12
50		Paint adhesion 2 hr	78	0	20	0
		strength 5 hr	95	0	58	12
		12 hr	99.9	0	93	29
55		24 hr	100	0	99.6	54

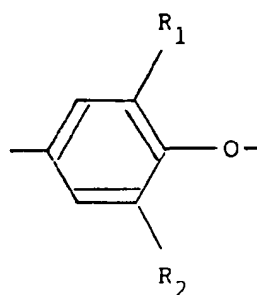
* Maleic anhydride

** Maleated EPR

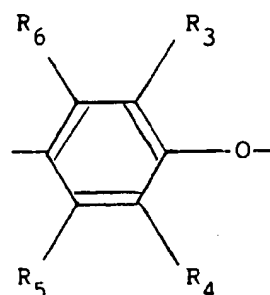
Claims

1. A thermoplastic composition comprising

(A) from 5 to 95 parts by weight of at least one polyphenylene ether which is a homopolymer or copolymer comprising repeating unit I and optionally repeating unit II



(I)



(II)

wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 are identical or different and each represents a monovalent residue with the proviso that R_3 and R_5 cannot be hydrogen simultaneously,

(B) from 95 to 5 parts by weight of at least one aliphatic polyamide and/or thermoplastic aromatic melt-polymerisable copolyamide containing as main component an aromatic amino acid and/or aromatic dicarboxylic acid,

(C) from 5 to 50 parts by weight based on 100 parts by weight of the total of polyphenylene ether and polyamide, of at least one elastomeric material obtainable by graft copolymerisation of

(a) from 50 to 90% by weight of at least one ethylene- α -olefin-(diene) copolymer and

(b) from 50 to 10% by weight of a grafting monomer mixture comprising

(i) at least one vinyl aromatic monomer and

(ii) at least one unsaturated functional monomer selected from unsaturated nitrile monomers and alkyl(meth)acrylates,

the total amount of unsaturated functional monomers being from 2 to 20% by weight of the total weight of the grafting monomer mixture, and

(D) from 0.01 to 30 parts by weight of at least one compatibilizing agent, based on 100 parts by weight of the total of the polyphenylene ether and polyamide.

2. A composition according to claim 1 wherein the polyphenylene ether is a poly(2,6-dimethyl-1,4-phenylene)ether, a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol, or a combination thereof.

3. A composition according to claim 1 or claim 2 wherein the polyamide is polyamide 6, polyamide 66, a blend of polyamide 6 and polyamide 66, a thermoplastic aromatic copolyamide, a blend of polyamide 6 and a thermoplastic aromatic copolyamide or a blend of polyamide 66 and a thermoplastic aromatic copolyamide.

4. A composition according to any one of claims 1 to 3 wherein the polyamide is present in an amount at least enough to form the continuous phase of the polyphenylene ether polyamide blend.

5. A composition according to any one of claims 1 to 4 wherein the vinyl aromatic compound is styrene.

6. A composition according to any one of claims 1 to 5 wherein the unsaturated functional monomer is acrylonitrile or an alkyl(meth)acrylate.

7. A composition according to any one of claims 1 to 6 wherein the ethylene- α -olefin-(diene) copolymer is selected from ethylene-propylene copolymers, ethylene-butene-1 copolymers, ethylene-propylene-ethylidene norbornene copolymers, ethylene-propylene-cyclopentadiene copolymers and ethylene-propylene-1,4-hexadiene copolymers.

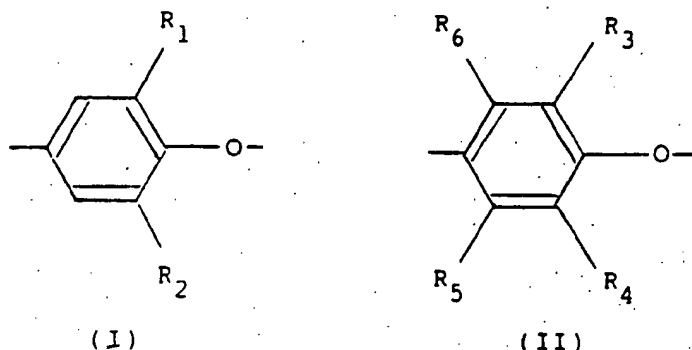
8. Substrate having improved impact strength and paint adhesion strength fabricated from a thermoplastic

composition according to any one of claims 1 to 7.

5 Patentansprüche

1. Thermoplastische Zusammensetzung umfassend

(A) 5 bis 95 Gewichtsteile mindestens eines Polyphenylenethers, welcher ein Homopolymer oder Copolymer ist, das eine sich wiederholende Einheit I und gegebenenfalls eine sich wiederholende Einheit II umfaßt



worin R₁, R₂, R₃, R₄, R₅ und R₆ identisch oder verschieden sind und jeweils einen einwertigen Rest darstellen, mit der Maßgabe, daß R₃ und R₅ nicht gleichzeitig Wasserstoff sein können,

(B) 95 bis 5 Gewichtsteile mindestens eines aliphatischen Polyamids und/oder thermoplastischen aromatischen schmelzpolymerisierbaren Copolyamids, das als Hauptkomponente eine aromatische Aminosäure und/oder eine aromatische Dicarbonsäure enthält,

(C) 5 bis 50 Gewichtsteile, bezogen auf 100 Gewichtsteile des gesamten Polyphenylenethers und Polyamids, mindestens eines elastomeren Materials, das erhältlich ist durch Pfropfcopolymerisation von

(a) 50 bis 90 Gewichtsprozent mindestens eines Ethylen- α -Olefin-(Dien)-Copolymers und

(b) 50 bis 10 Gewichtsprozent einer Pfropfmonomermischung umfassend

(i) mindestens ein aromatisches Vinylmonomer und

(ii) mindestens ein ungesättigtes funktionelles Monomer, das ausgewählt ist aus ungesättigten Nitrilmonomeren und Alkyl(meth)acrylaten,

wobei die Gesamtmenge an ungesättigten funktionellen Monomeren 2 bis 20 Gewichtsprozent des Gesamtgewichts der Pfropfmonomermischung beträgt, und

(D) 0,01 bis 30 Gewichtsteile mindestens eines Kompatibilisierungsmittels, bezogen auf 100 Gewichtsteile des gesamten Polyphenylenethers und Polyamids.

2. Zusammensetzung nach Anspruch 1, worin der Polyphenylenether ein Poly(2,6-dimethyl-1,4-phenylen)ether, ein Copolymer von 2,6-Dimethylphenol und 2,3,6-Trimethylphenol oder eine Kombination davon ist.

3. Zusammensetzung nach Anspruch 1 oder Anspruch 2, worin das Polyamid Polyamid 6, Polyamid 66, eine Mischung von Polyamid 6 und Polyamid 66, ein thermoplastisches aromatisches Copolyamid, eine Mischung von Polyamid 6 und einem thermoplastischen aromatischen Copolyamid oder eine Mischung von Polyamid 66 und thermoplastischem aromatischem Copolyamid ist.

4. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 3, worin das Polyamid mindestens in einer Menge vorhanden ist, die ausreicht, um eine kontinuierliche Phase der Polyphenylenether-Polyamid-Mischung zu bilden.

5. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 4, worin die aromatische Vinylverbindung Styrol ist.

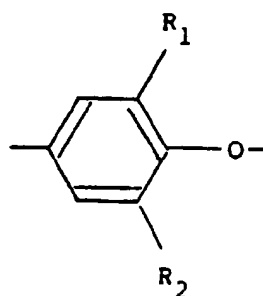
6. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 5, worin das ungesättigte funktionelle Mono-

mer Acrylnitril oder ein Alkyl(meth)acrylat ist.

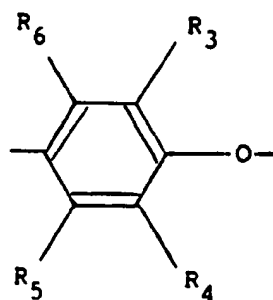
7. Zusammensetzung nach irgendeinem der Ansprüche 1 bis 6, worin das Ethylen- α -Olefin-(Dien)-Copolymer ausgewählt ist aus Ethylen-Propylen-Copolymeren, Ethylen-Buten-1-Copolymeren, Ethylen-Propylen-Ethylidennorbornen-Copolymeren, Ethylen-Propylen-Cyclopentadien-Copolymeren und Ethylen-Propylen-1,4-Hexadien-Copolymeren.
8. Aus einer thermoplastischen Zusammensetzung nach irgendeinem der Ansprüche 1 bis 7 hergestelltes Substrat mit verbesserter Schlagbiegefestigkeit und Farbhaftefestigkeit.

Revendications

1. Composition thermoplastique comprenant
(A) de 5 à 95 parties en poids d'au moins un poly(oxyde de phénylène), qui est un homopolymère ou un copolymère comprenant un motif répétitif I et éventuellement, un motif répétitif II



(I)



(II)

dans lesquels R₁, R₂, R₃, R₄, R₅ et R₆ sont identiques ou différents et représentent chacun un radical monovalent, sous réserve que R₃ et R₆ ne peuvent pas être simultanément de l'hydrogène,

(B) de 95 à 5 parties en poids d'au moins un polyamide aliphatique et/ou d'un copolyamide aromatique thermoplastique polymérisable par fusion et contenant, comme constituant principal, un acide aminé aromatique ou un acide dicarboxylique aromatique,

(C) de 5 à 50 parties en poids pour 100 parties en poids de la somme du poly(oxyde de phénylène) et du polyamide, d'au moins une matière élastomère, qui peut être obtenue par copolymérisation par greffage de

(a) 50 à 90 % en poids d'au moins un copolymère éthylène- α -oléfine-(diène) et

(b) 50 à 10 % en poids d'un mélange de monomères de greffage comprenant

(i) au moins un monomère vinylaromatique et

(ii) au moins un monomère fonctionnel insaturé choisi parmi les monomères nitriles insaturés et les (méth)acrylate d'alcoyle,

la quantité totale de monomères fonctionnels insaturés représentant de 2 à 20 % du poids total du mélange de monomères de greffage, et

(D) de 0,01 à 30 parties en poids d'au moins un agent de compatibilité pour 100 parties en poids de la somme du poly(oxyde de phénylène) et du polyamide.

2. Composition suivant la revendication 1, dans laquelle le poly(oxyde de phénylène) est un poly(oxyde 2,6-diméthyl-1,4-phénylène), un copolymère de 2,6-diméthylphénol et de 2,3,6-triméthylphénol ou leurs combinaisons.
3. Composition suivant la revendication 1 ou 2, dans laquelle le polyamide est du polyamide 6, du polyamide 66, un mélange de polyamide 6 et de polyamide 66, un copolyamide aromatique thermoplastique, un mélange de polyamide 6 et d'un copolyamide aromatique thermoplastique ou un mélange de polyamide 66 et d'un copolyamide aromatique thermoplastique.

4. Composition suivant l'une quelconque des revendications 1 à 3, dans laquelle le polyamide est présent en une quantité au moins suffisante pour former la phase continue du mélange de poly(oxyde de phénylène) et de polyamide.
5. Composition suivant l'une quelconque des revendications 1 à 4, dans laquelle le composé vinyl-aromatique est le styrène.
6. Composition suivant l'une quelconque des revendications 1 à 5, dans laquelle le monomère fonctionnel insaturé est l'acrylonitrile ou un (méth)acrylate d'alcoyle.
7. Composition suivant l'une quelconque des revendications 1 à 6, dans laquelle le copolymère éthylène- α -oléfine-(diène) est choisi parmi les copolymères éthylène-propylène, les copolymères éthylène-butène-1, les copolymères éthylène-propylène-éthylidène norbornène, les copolymères éthylène-propylène-cyclopentadiène et les copolymères éthylène-propylène-1,4 hexadiène.
8. Substrat ayant de meilleures résistances aux chocs et résistance à l'adhérence de la peinture, fabriqué en une composition thermoplastique selon l'une quelconque des revendications 1 à 7.